# *DEVELOPMENTS IN THE SIMTECHE PROCESS*
# *$CO_2$ CAPTURE BY FORMATION OF HYDRATES*

**Presented to**

**The Third Annual Conference on Carbon Capture and Sequstration**

**Washington DC**

**May 3-6, 2004**

# Presentation Outline

- Background
- Objectives
- Accomplishments
- Experimental Program
- Engineering Analysis
- Program Status

# $CO_2$ Hydrate Program – Team Members

DOE/NETL Project Manager – José Figueroa

Program Funding – Gary Steigel, Scott Klara

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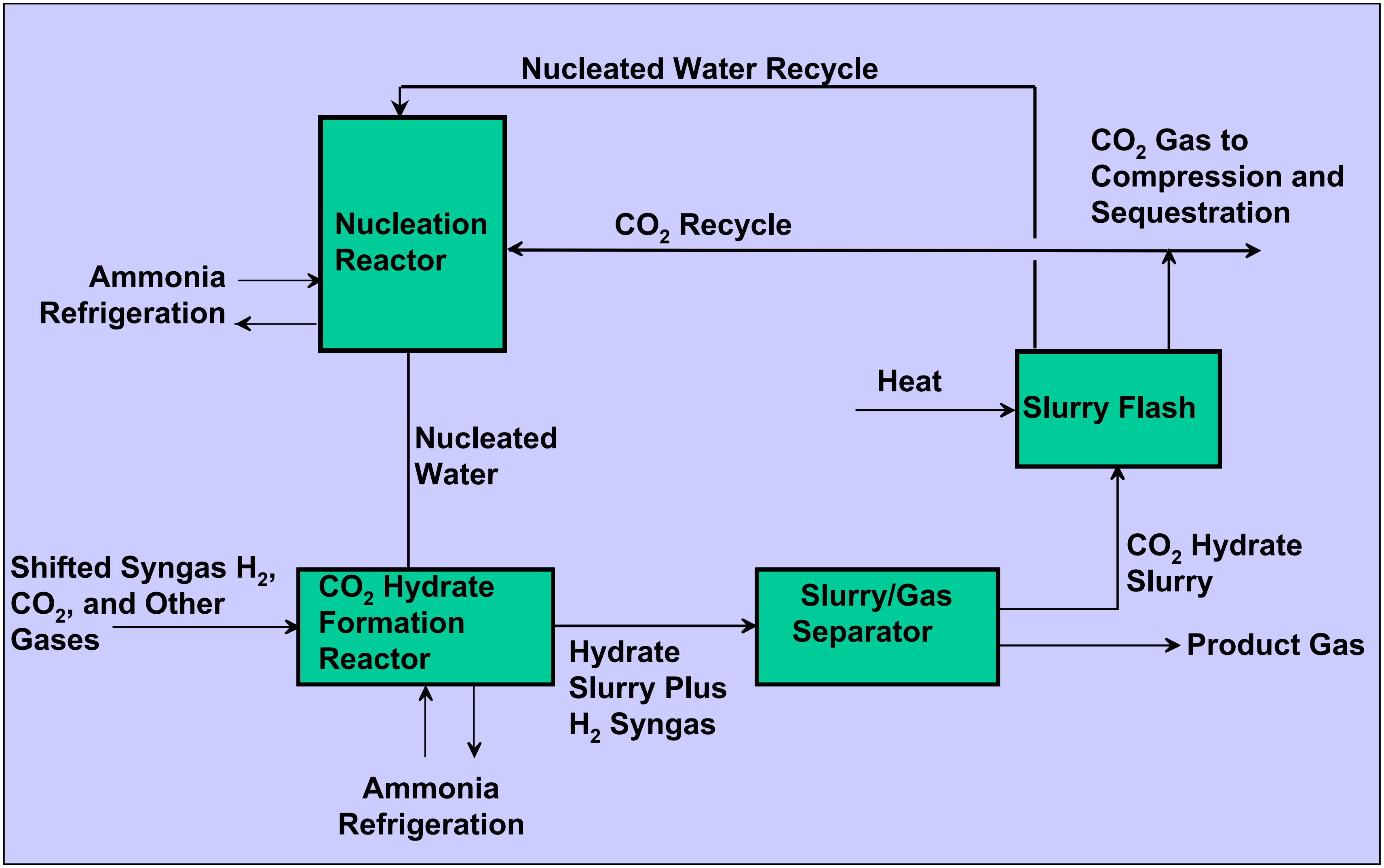
*SIMTECHE*

# Simteche Block Flow Diagram



# *Program Plan*

- **Three Phases**
  - **Phase 1 – Proof-of-Concept**
  - **Phase 2 – Develop Scale-up Data, Design, and Build Slip-Stream Pilot Plant**
  - **Phase 3 –Tests at Operating Gasification Plant**

# Objectives

- **Phase 2 Objectives**
  1. **Engineering Test Model**
     - Develop Design Data on Unit Operations
     - Argon/$CO_2$ Mixtures
  2. **Hydrogen Flow Tests**
     - Demonstrate Separation in Hydrogen with $H_2S$
  3. **Design Slipstream Test Unit (STU)**
     - Skid-Mounted
     - Demonstration on Slipstream From Operating Gasifier

- **Phase 3 Objectives : Demonstrate Operation**

# *Accomplishments – Phase 2*

- **Improved Separation Prediction**
  - Correlations and calculation methods developed
- **ETM Unit Designed-Built-Operational**
  - Lessons Learned Incorporated
- **Hydrogen Flow System Relocated – Validated**
  - Initial Flow Tests Done
  - Consistency with $Ar/CO_2$ Results Established
- **STU Site Selected**
  - TECO Polk Power Plant
  - Costs Estimated
  - Design Basis Established

# Cost Targets

- Current Estimate - \$9 per ton of $CO_2$
- Target 1 - \$5 per ton of $CO_2$
  - Minimum 75% Removal
- Target 2 - \$10 per ton of $CO_2$
  - 90+% Removal
- Basis
  - 2200 Psig Pipeline Pressure
  - High-Pressure Gasifier
- Revised Economic Analysis in Progress

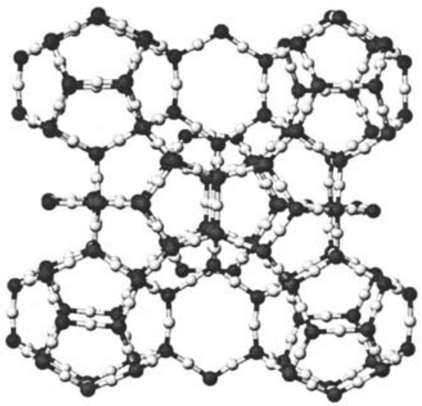
# *Revised Economic Analysis*

- **Incorporates NETL Analysis Standards (Developed By Scott Klara)**
  - All Technologies Compared on an Equal Basis
  - Comparison to Conventional Technologies
  - Incorporated into IGCC with Shift Reaction
  - Benchmark for All Cases: H-Class Gas Turbine
- **Design Cases**
  - Once-Thru: 70+% minimum removal
  - 2 Promoter Cases to Enhance Removal to 90%
  - Once-Thru plus Selexol to Enhance Removal to 90%

# *Technology Development Roadmap*

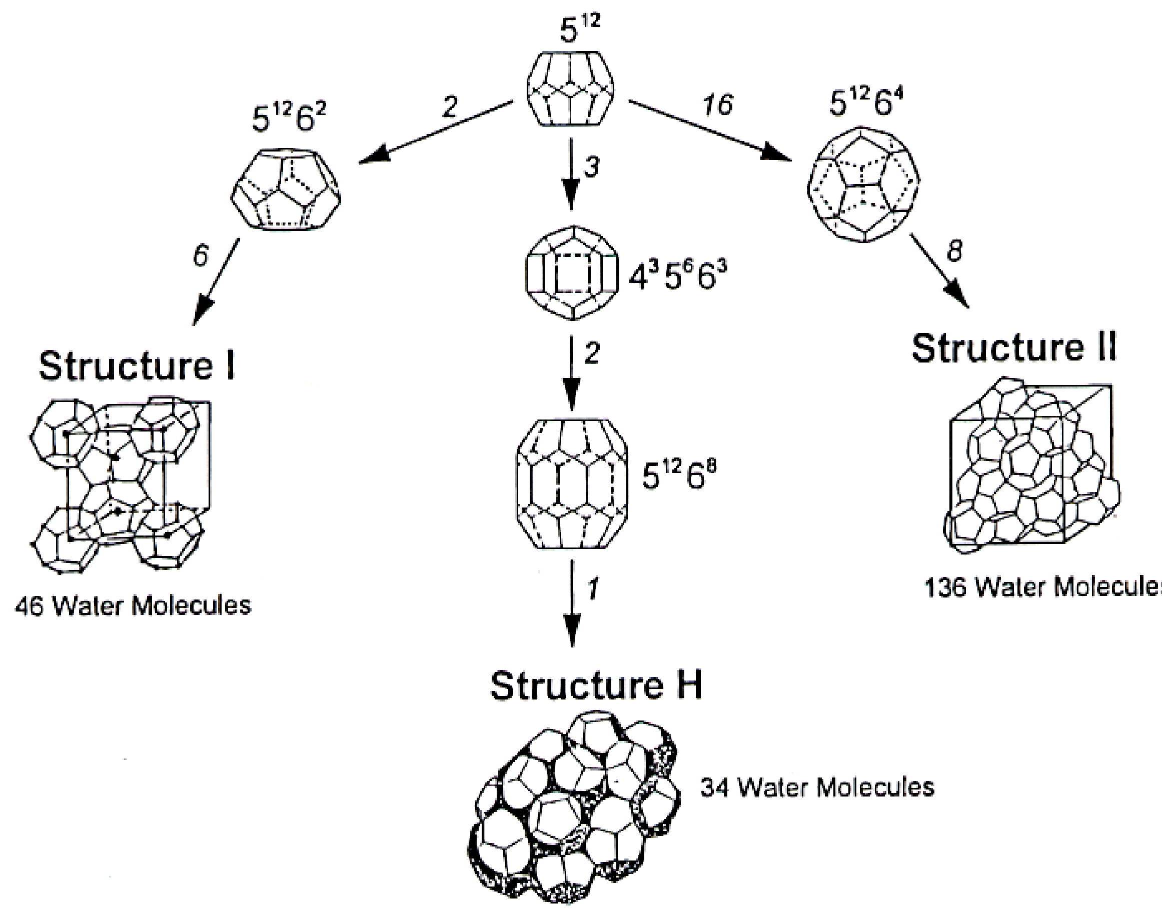
- **Currently, configured only for high-pressure gasifiers**
  - **the commercial success depends on the number of gasifiers being built**
- **Promoters are being investigated for low-pressure (flue-gas) $CO_2$ capture, which broadens the market immensely**

# *Ice-like Gas Hydrates*



Water Structure in the sI Hydrate
Guest Molecules (not shown) fit
Within the polyhedral cages.

**BASIS OF SEPARATION**
- **$CO_2/H_2S$ Form sI Hydrate**
- **$H_2$ Too Small to Stabilize the Water Cages**



# EXPERIMENTAL ACTIVITIES
## (JUNE 03- MARCH 04)

- **BENCH SCALE RIG ($H_2/CO_2$; $H_2/CO_2/H_2S$)**
- **E.T.M. COMPLETION AND COMMISSIONING**
- **PHASE BEHAVIOR; PROMOTER TESTING**

# BENCH SCALE FLOW TESTS ($H_2/CO_2$; $H_2/CO_2/H_2S$)

- USE OF SURROGATE MIXES ($CO_2$/Ar; $CO_2$/He) VALIDATED USING $H_2/CO_2$ MIXTURES
- SUCCESSFUL $H_2/CO_2$ RUNS OVER THE RANGE OF 700-1000 psi
- SIMULATED SYNTHESIS GAS ($H_2/CO_2/H_2S$) EXPERIMENTS

# $H_2/CO_2/H_2S$ FLOW TESTS

- **DEPLETION OF $H_2S$ IN THE GAS RELATIVE TO $CO_2$**

  **Mass Transfer Limited: rate ~ $k_m(C_g - C_{eq})$**

  **Analysis of mass flux-limited hydrate growth suggests hydrate can be enriched in $H_2S$ (relative to the initial gas composition) but to an extent *less than* that measured in the equilibrium hydrate.**

  **Kinetically Limited: rate ~ $k\,(f_l - f_{MHF})$**

  **Fugacity of $CO_2$ relative to its fugacity at minimum hydrate formation condition is much higher than the fugacity of $H_2S$ Relative to its minimum hydrate formation fugacity.**

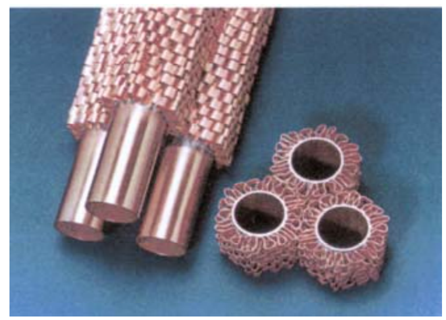
- **EXPERIMENTAL SEQUENCE**

  **Produce hydrate from initial gas mix. Analyze off-gas.**
  **Repeat using off-gas composition and end pressure as feed.**
  **Continue until equilibrium conversion reached.**
  **Compare final pressure and vapor composition to equilibrium measurements/calculations.**

# ENGINEERING TEST MODULE (ETM)

- REMOVE LIMITATIONS OF BENCH SCALE UNIT

  - ADDITIONAL FINNED TAIL TUBE
  - ENHANCED PROCESS COOLING SYSTEM
  - ADDITIONAL INSTRUMENTATION
  - ENHANCED WATER FEED SYSTEM



- PROVIDE ADDITIONAL DATA FOR PILOT PLANT DESIGN

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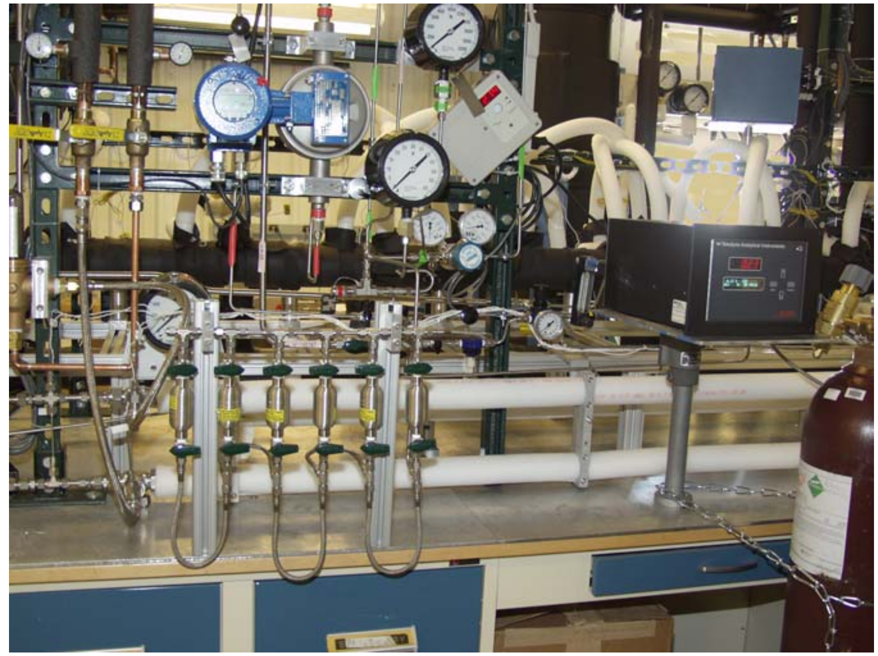

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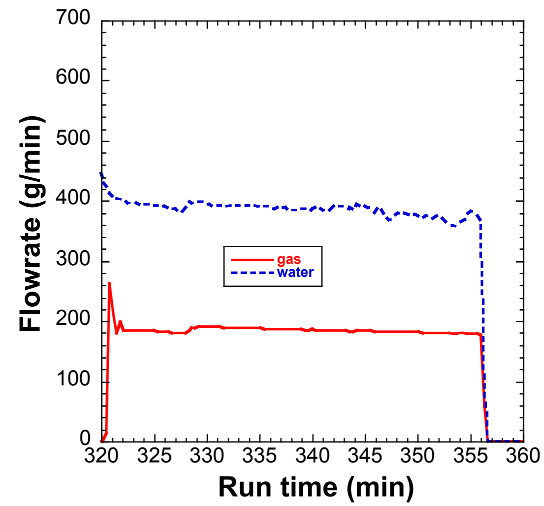
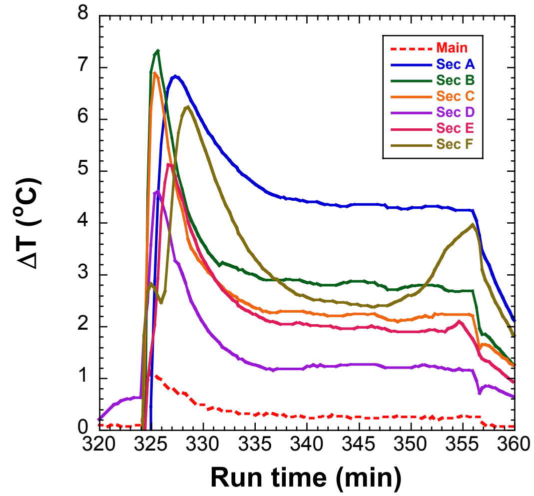
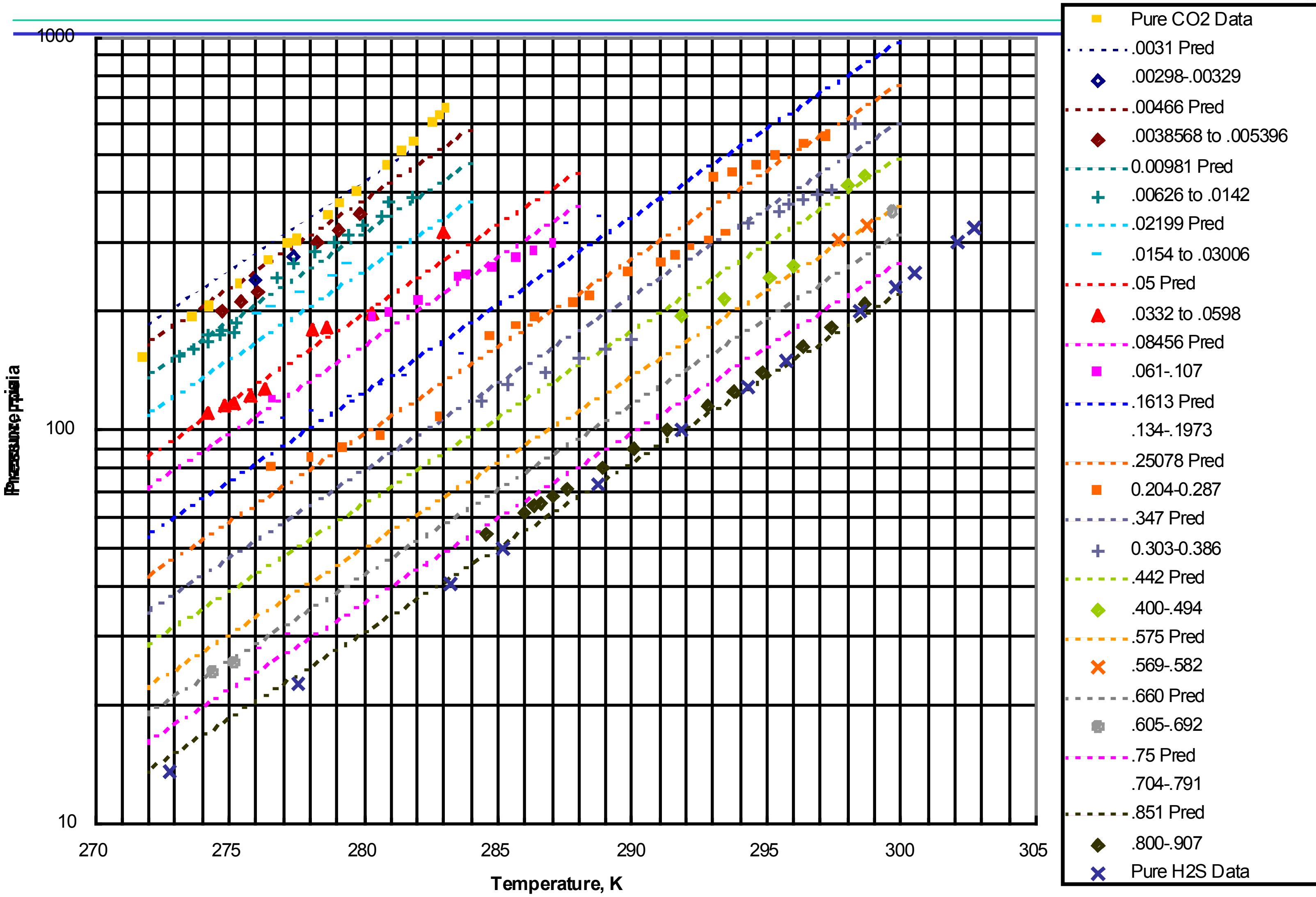


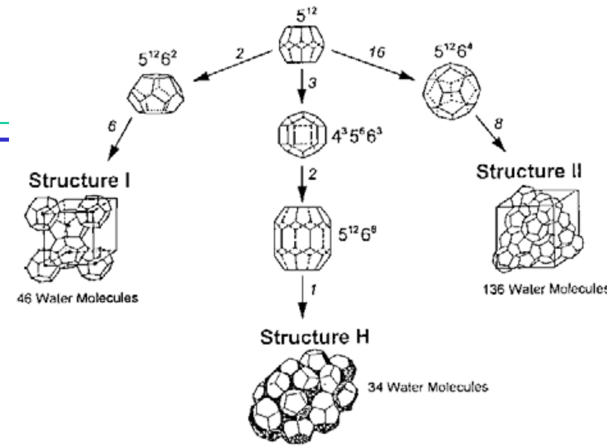

## SYSTEM SHAKE-OUT:

- START-UP PROCEDURE DEVELOPED
- SEVERAL RUNS 30 MIN. OR MORE
- RUNS AT HIGH GAS/LIQUID RATIOS
- QUANTITATIVE RESULTS IMMINENT

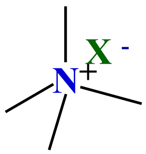
# PHASE EQUILIBRIUM



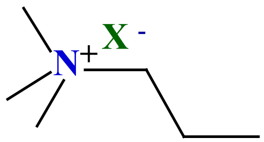
# PROMOTER DESIGN AND TESTING



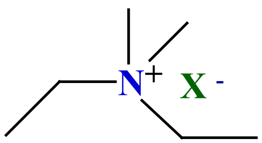

**IDEA: Employ Non-volatile Salt Analogs of common sH-formers**



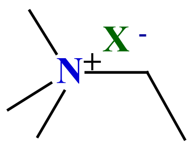

"Isopentane"



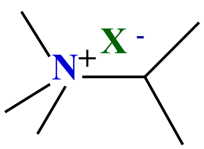

"2,2-Dimethyl pentane"




"3,3-Dimethyl pentane"




"2,2-dimethyl butane"




"2,2,3-Trimethyl butane"

**Example of "Promoter" effect:**

**(Mehta, A. P., Ph. D. Thesis, Colorado School of Mines, 1996)**

**Methane requires 370 psi to form sI clathrate at 273K.**

**Methane-containing sH clathrate forms at just 140 psi with 2,2,3-Trimethyl butane (273K).**

***Salt analogs synthesized and undergoing testing with key constituents: $CO_2$ and $CO_2/H_2S$***